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**EFFECT OF IONIZING RADIATION ON
COMBUSTION OF AMMONIUM PERCHLORATE
AND MIXTURE SYSTEMS OF THE LATTER**

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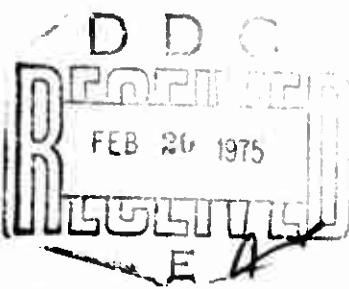
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ABSTRACT: Ammonium perchlorate and mixtures of it were studied for the effect of ionizing radiation. Various types of ionizing radiation showed the effect on the combustion of ammonium perchlorate of different pressures and temperatures. The results obtained agreed with the theories held on the role of processes taking place in the condensed zone and on determining the combustion rate.



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One of the basic questions on the combustion theory of condensed systems with an ammonium perchlorate base is that of the limiting stage of combustion. Its solution is complicated by the fact that ammonium perchlorate during combustion undergoes a series of different physicochemical transformations. An exothermal decomposition reaction takes place in the condensed phase. Simultaneously, ammonium perchlorate is sublimated and dispersed from the combustion surface as the result of the liberation and eflux of gases -- products of thermal decomposition of condensed substance. Finally, the combustion process is completed in the gas phase.

Let us analyze first of all the effect of reaction in the condensed phase and phenomena which accompany it (sublimation, dispersion), during the combustion process. The expression for the combustion rate in this case (without allowing for the heat flux from the gas zone) is described in the following way [1].

$$u^2 = \frac{k_0 \lambda R T_f^2}{I_0 Q_0 Q E} e^{-\frac{E}{R T_f}},$$

$$I_0 = \int_0^{\eta_f} \frac{\eta_f - \eta}{I(\eta)} d\eta; \quad T_n = T_0 + \frac{Q}{c} \eta_f. \quad (1)$$

$I_0 = \eta_f + (1 - \eta_f) \ln(1 - \eta_f)$ -- for a reaction of the first order.

By designating: u -- the combustion rate; k_0 , E -- the kinetic parameters; λ , ρ_0 , Q , c -- thermophysical constants; T_f -- the temperature on the combustion surface; η_f -- the depth of decomposition of substance on the

surface; $f(\eta)$ -- the function, determining the type of chemical kinetics, ($f(\eta) = 1 - \eta$ for a reaction of the first order).

Sublimation and dispersion reduce the depth of exothermal decomposition of substance η_f on the combustion surface, and by the same token, have a dual effect on its rate. On one hand, as all processes for forced mechanical removal of substance from a surface, they increase the spreading speed of the reaction front, which is reflected in formula (1) of the inverse relationship of u on I_0 . On the other hand, sublimation and dispersion cause a reduction of temperature of the combustion surface and, consequently, a reduction of the combustion rate. Since the latter relationship is stronger owing to its exponential nature, the combustion rate is reduced with an increase in the amount of sublimated or dispersed substance. Analysis of the dispersion effect was first carried out by A. G. Merzhanov [2].

When there is sublimation on the combustion surface, the following correlations are true:

Thermal balance

$$T_f = T_0 + \frac{Q}{c} \eta_f - \frac{Q_c}{c} (1 - \eta_f); \quad (2)$$

Material balance

$$\eta_f + \eta_c = 1; \quad p = p_f + p_c. \quad (3)$$

where p -- ambient pressure;

p_f -- partial pressure of decomposition products of condensed substance;

p_c -- pressure of saturated steam of the initial substance;

η_c -- the amount of sublimated substance;

Q_c -- the heat of sublimation;

Q -- decomposition

By using the obvious relationship

$$\frac{p_f}{p_c} = \frac{r_f \eta_f}{r_c \eta_c},$$

where r_f and r_c -- the number of mol formed during decomposition and sublimation of mol of initial substance respectively, and the dependence of p_c on T_f in the form $p_c = B \exp\left(-\frac{L}{RT_f}\right)$, we obtain a link between p and η_f

$$p = \left[1 + \frac{r_f \eta_f}{r_c (1 - \eta_f)} \right] B e^{-\frac{L}{RT_f}}, \quad (4)$$

in which the value of T_f is determined by the relationship (2).

This expression makes it possible to determine the dependence of combustion rate on ambient pressure together with formula (1). The pressure coefficient $\nu = \frac{\partial \ln u}{\partial \ln p}$ is written in the following form:

$$\nu = \left[\frac{E}{2RT_f} + \frac{1}{T_f} - \frac{c}{2jQI_0} \cdot \frac{\partial I_0}{\partial \eta_f} \right] \alpha \left(1 + \frac{aL}{RT_f} \right)^{-1}, \quad (5)$$

where

$$z = \frac{1Q}{c} (1 - \eta_f) \left[\eta_f + \frac{r_c}{r_f} (1 - \eta_f) \right];$$

$$j = 1 + \frac{Q_c}{Q};$$

$$I_0 = \eta_f + j (1 - \eta_f) \ln (1 - \eta_f) \quad \left. \begin{array}{l} \\ \frac{\partial I_0}{\partial \eta_f} = 1 - j - j \ln (1 - \eta_f) \end{array} \right\} \begin{array}{l} \text{for reaction of the} \\ \text{first order} \end{array}$$

In formula (5) the second and third terms in the first bracket are small and can be disregarded. If $\frac{aL}{RT_f^2} \gg 1$, that is, when there is a large value of evaporation heat L , $\nu = \frac{E}{2L}$, which coincides with an expression earlier obtained by Ya. B. Zel'dovich without allowing for gassing and thermal decomposition of substance 3. Calculations by these formulas show that when ambient pressure is increased, the combustion rate decreases, the amount of decomposed substance increases, and the amount of sublimated substance decreases respectively. The pressure coefficient ν

changes little. When $p \rightarrow \infty$, $\eta_f \rightarrow 1$, $\gamma \rightarrow 0$ and $u \rightarrow \text{const.}$

The expression for the temperature coefficient $\beta = \frac{\partial \ln u}{\partial T_0}$ has the form

$$\beta = \left[\frac{E}{2RT_f^2} + \frac{1}{T_f} + \frac{aL}{RT_f^2} \cdot \frac{c}{2jQI_0} \cdot \frac{\partial I_0}{\partial \eta_f} \right] \left(1 + \frac{aL}{RT_f} \right)^{-1} \quad (6)$$

In this formula the second term in the first bracket is small, but the third one is quite large. If $r_f = 0$ (thermal decomposition occurs without gassing), then $a \rightarrow \infty$. Then for reaction of a zero order $[I(\gamma) = 1: I_0 = \frac{1}{2} \eta_f^2; \frac{\partial I_0}{\partial \eta_f} = \eta_f \text{ when } j = 1]$, Formula (6) assumes the form $\beta = \frac{E}{Q\eta_f} = \frac{1}{T_f - T_0}$, which corresponds with an expression for β in the Zel'dovich model [3].

The dispersion process in the case of solid non-melting substances is determined by many factors, which cannot be accurately calculated at the present time.

However, on the basis of examining simple physical relationships one can obtain a dependence of combustion rate on ambient pressure and some other factors as a result of dispersion.

We shall examine the mechanism for the occurrence of dispersion. Force F , proportional to the pressure gradient, acts upon solid particles of a decomposing substance from an outgoing gas flow.

$$F = \frac{\partial p}{\partial x} \cdot d,$$

where d -- particle size.

The pressure gradient is linked with the filtration rate of gas in vapors by the Darcy law [4].

$$u_\phi = \frac{c_\phi}{\mu} \cdot \frac{\partial p}{\partial x},$$

where u_f -- the filtration rate;

c_f -- permeability;

μ -- viscosity.

By taking note of the continuity equation of flow $u_f \rho_f = \eta \rho_0 u$

(u -- combustion rate; ρ_0 -- the density of a solid substance; ρ_g -- the density of gas; η -- the depth of decomposition) and the ratio $\rho_g = R_p/RT$, we obtain

$$F = \frac{\mu dRT \eta \rho_0}{c_f M} \cdot \frac{u}{p}.$$

The dispersion moment, that is, the destruction of the condensed zone, like the ejection of particles, will be determined by the equality of force F to the force keeping the substance from destruction, that is, its stability H . Then, we have

$$u = \frac{c_f H M}{\mu d R T \eta_f \rho_0} p. \quad (7)$$

In this formula, a series of values (permeability, strength, etc) depends on η_f . In the general case, this dependence can be shown by a function

$$\psi = \eta_f^k (1 - \eta_f)^l, \quad \text{where } k \text{ and } l \text{ are positive or negative numbers.}$$

Apparently, the dependence of ψ on η_f should not be strong, since for example the increase of permeability c_f with the increase of η_f is partially compensated by the reduction of strength H . By comparing formulas (1) and (7) it follows that the value of η_f is expressed by a weak logarithmic dependence on p . Consequently, it can be calculated that function ψ depends little on pressure and, the combustion rate of dispersing substances should depend linearly on ambient pressure. This conclusion concurs with experimental data, according to which solid explosives for which the dispersion is most characteristic (for example, fulminate of mercury and several other initiating explosives) have, at least at low pressures, a linear combustion

law [5]. Dispersion was examined in more detail in a work by B. I. Khaykin and A. G. Merzhanov [6].

From this analysis, it follows that in this case when reaction of exothermal decomposition of a substance occurs during combustion, the removal process of the initial substance (sublimation, dispersion) has a significant effect on the combustion process. Firstly, it reduces the combustion rate and secondly because of it the combustion rate begins to depend on pressure.

In order to test the role of reaction in the condensed phase and removal processes of a substance in the case of ammonium perchlorate, we studied the effect of ionizing radiation on combustion rate, since preliminary irradiation of a substance as opposed to the normal methods of influence, for example, using catalyzing additives, makes it possible to change the reaction rate of thermal decomposition of a substance, without acting upon other characteristics of the system, for example, on the gas-phase reaction. By using volumetric or surface irradiation and, by the same token, changing the topography of decomposition reaction in crystals of ammonium perchlorate, one can also simultaneously influence the dispersion process.

The experiment

Research into the kinetics of thermal decomposition of ammonium perchlorate, conducted by the weight method by the authors together with Yu. I. Rubtsov, showed that when affected by preliminary irradiation (X-ray, electrons with an energy of 1.6 MeV, glow discharge plasma) the decomposition of ammonium perchlorate significantly increases, proportional to the irradiation dose.

Experiments on the combustion of specimens of ammonium perchlorate and mixtures of it with combustibles were carried out beforehand with an irradiated substance, and by direct irradiation of the hot zone at the moment of combustion of the specimens. The combustion rate was determined by photorecording the flame or measuring the combustion time of the fixed section of specimens in a constant pressure bomb with an electric second timer. Ammonium perchlorate of three fractional compositions was used: 50, 50 - 100 and 100 - 250 μ m. It was compressed in thin-walled tubes made from stainless steel with an internal diameter of 6.2 mm. Mixtures with fuels were prepared without a casing (specimen diameter, 8 mm). The tests were made at different initial temperatures (up to 250°C) and ambient pressures (up to 60 atm).

During the experiments, a study was made of the effect of ionizing radiation with different penetrating powers: X-rays, a fast electron beam, glow discharge plasma. Irradiation by fast electrons ($E = 1.6$ MeV) was carried out with an accelerator, and the specimens of compressed ammonium perchlorate were placed below its beam. The specimens were irradiated with doses of 300 - 400 mrad, and subsequent combustion of them at initial temperatures of 20 - 250°C and pressures of 10 - 60 atm* showed that the effect of irradiation, basically, reduces the temperature limit of self-sustaining combustion and the combustion rate changes little. The effect of irradiation only occurs at small pressures (10 and 20 atm).

Figure 1 shows the rate-initial temperature relationship at a pressure of 10 atm* for ammonium perchlorate with a particle size of 50 - 100 μ m. The limit of self-sustaining combustion when affected by an irradiation dose of 400 mrad is reduced from 160 to 80°C. The decrease in particle size of ammonium perchlorate reduces the effect of irradiation (Figure 2).

* [Note: atm = atmospheric overpressure.]

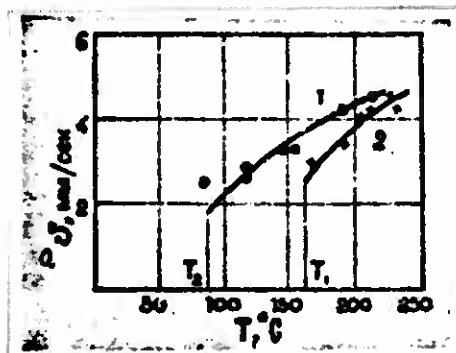


Fig. 1. The dependence of combustion rate of ammonium perchlorate on the initial temperature when $p = 10$ atu (fraction 50 - 100 μm): 1 -- specimens irradiated with electrons (a dose of 400 mrad); 2 -- control specimens.

Key: a. mm/sec

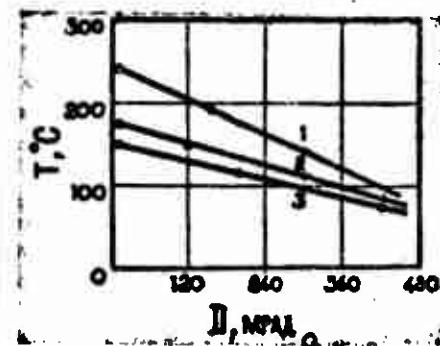


Fig. 2. The dependence of the temperature limit of self-sustaining combustion on the irradiation dose when $p = 10$ atu: 1 -- fraction 100 - 250 μm ; 2 -- fraction 50 - 100 μm ; 3 -- fraction 50 μm .

Key: a. mrad

Experiments to study the effect of ionizing radiation during combustion of specimens were conducted in a device, the diagram of which is shown in Figure 3. A beam of electrons with an energy of 1.6 MeV was directed from

an accelerator, using rotary magnets, through a thin metal foil to the combustion area. The combustion surface was maintained at a constant level with a supporting needle and an ejecting spring. The dose rate was calculated according to the current density of electrons on a commutator beyond the irradiated combustion zone. While the specimen was under the beam, the irradiation dose during combustion was ~ 1 mrad. These experiments showed that during combustion of ammonium perchlorate and mixtures of it with different combustibles during irradiation at pressures up to 10 atu and an initial temperature up to 250°C changes in the combustion rate do not occur.

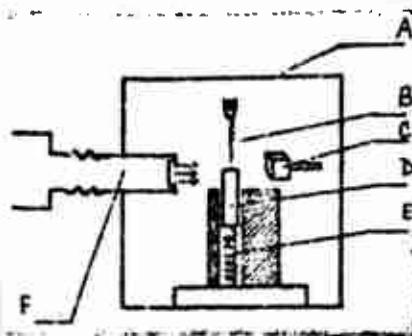


Fig. 3. A diagram of the equipment for irradiating specimens during the combustion process: (A -- body of the bomb; B -- needle; C -- commutator; D -- specimen; E -- spring; F -- pipe connection for an electron input)

Similar information was also obtained when studying the effects of preliminary irradiation by X-ray with a dose of ~ 1 mrad on the combustion of ammonium perchlorate.

In order to irradiate the substance only on the surface layers, a powder of ammonium perchlorate was placed in the zone of the high-frequency

glow discharge in argon at a pressure of ~ 1 mmHg. The vessel containing the substance was cooled by liquid nitrogen and continually shaken. During discharge, the active particles (electrons, ions, etc) only affect the surface layers of ammonium grains since the electron energy, apparently, does not exceed several tens of electron volts.

During the combustion of specimens, prepared from powder irradiated in this way, at a pressure of 10 atu there is a reduction in the temperature limit of self-sustaining combustion. Treatment of the powder in plasma for several minutes would have been equivalent to irradiation by fast electrons with a dose of 100 mrad. At a pressure of 40 atu, surface irradiation in glow discharge plasma as opposed to experiments with fast electrons, showed a significant increase of combustion rate (by 20 - 25%) over the whole investigated range of initial temperatures (Figure 4). Storing the specimens of irradiated ammonium perchlorate for ten days did not cause any noticeable change.

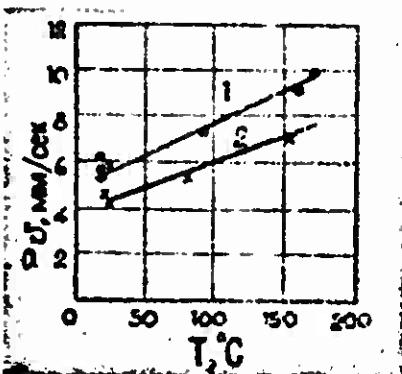


Fig. 4. The dependence of combustion rate of ammonium perchlorate on the initial temperature when $p = 40$ atu (fraction 50 - 100 μm): 1 -- irradiation of a powder in a discharge plasma; 2 -- without irradiation

Key: a. mm/sec

The effect of preliminary treatment of ammonium perchlorate in a plasma also caused the increase of the combustion rate of a stoichiometric mixture of it with polypropylene by 20% at a temperature of 40 atm and room temperature.

Discussion of results

The information obtained on the effect of preliminary irradiation of ammonium perchlorate on combustion rate, in our opinion, clearly shows the important role of processes taking place in the condensed combustion zone. The greatest effect is obtained for poorly penetrating radiation -- in glow discharge plasma. This feature has a natural explanation in the complex mechanism of radiation effect. Radiolysis of ammonium perchlorate crystals increases the thermal decomposition rate of a substance and, as a consequence, the dispersion process of crystals during combustion is intensified. From formulas (1) and (?) it follows that the combustion rate in a model with dispersion depends on activation energy according to a power law, on the multiplier logarithmically, that is, the dependence of combustion rate on the kinetic parameters is reduced. If the whole volume of the crystal is irradiated, as took place with rapid electrons and X-rays, as a result of the interference of these factors, the combustion rate is practically unchanged. Only when there are large irradiation doses (300 - 400 mrad) is there a reduction of the temperature limit in small pressures, and a small increase in the combustion rate. Obviously, in extreme combustion conditions, the relative role of kinetic acceleration, caused by radiation, is especially important. The decrease of irradiation effect with the reduction of ammonium perchlorate particle size, apparently, is linked with the increased role of "natural" defects in finely dispersed powder with respect to defects occurring during irradiation. When the dose is increased to 400 mrad, the level of

imperfection in crystals of different fractional composition becomes identical, and causes almost one and the same limiting temperature value of self-sustaining combustion (Fig. 2).

Surface irradiation of ammonium perchlorate grains (in discharge plasma), during subsequent combustion of specimens, causes an increased reaction on the surface of grains, but, apparently, does not affect the dispersion rate --- this can explain the observed increase of combustion rate in this case.

This effect is identical for ammonium perchlorate and its mixtures with combustibles. This shows the important role of decomposition kinetics of ammonium perchlorate for the combustion process of mixture compositions.

Conclusions

1. Analysis was made of the effect of reaction in the condensed phase and the phenomenon of removal of a substance (sublimation, dispersion) on the combustion rate.

2. The effect of different types of ionizing radiation was studied on the combustion of ammonium perchlorate and its mixtures with combustibles at different pressures and initial temperatures.

3. The results obtained agree with theories on the important role of processes taking place in a condensed zone, and in establishing combustion rate.

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